A complete basis set model chemistry for excited states

George A. Petersson

Hall-Atwater Laboratories of Chemistry,

Wesleyan University,

Middletown, Connecticut 06459-0180

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John Pople's Model Chemistries

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The CBS-Q//B3 Model

Geometry: B3LYP/6-311G(2d,d,p)

ZPE & Thermal: B3LYP/6-311G(2d,d,p)

SCF: UHF/6-311+G(3d2f,2df,2p)

CBS(extrap) - MP2: UHF/6-311+G(3d2f,2df,2p)

MP3, MP4(SDQ): MP4(SDQ)/6-31+G(d(f),d,p)

MP5 - CCSD(T): CCSD(T)/6-31+G(d')

Empirical Corrections:

$-5.79\ mE_h\ |S|^2_{ii}[\Sigma_i C^2_{\mu}]_{ii}$ (2e $^-$)

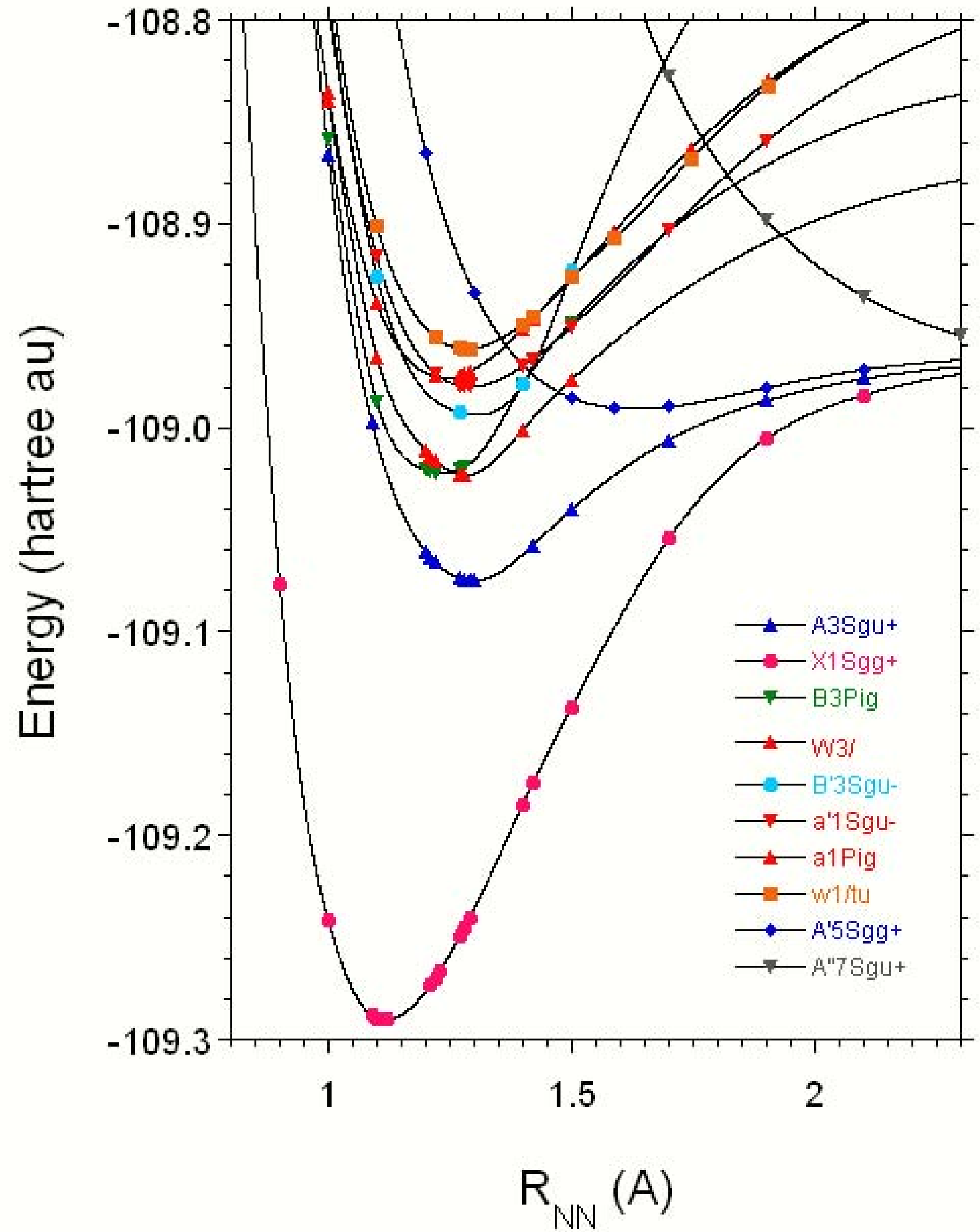
$-9.54\ mE_h\ \Delta(S^2)$ (Spin Contam.)

$E(core) \sim 3.92\ mE_h\ Q_{Na} + 2.83\ mE_h\ Q^2_{Na}$

Experimental Atomic Spin-Orbit Interaction

Test Case

The $X\,^1\Sigma_g^+$ ground state, along with the $a\,^3\Sigma_u^+$, $A'\,^5\Sigma_g^+$, and $A''\,^7\Sigma_u^+$ excited states of **N_2 dissociates to two $^4S_{3/2}$ ground state N atoms. Other low-lying singlet and triplet states dissociate to N atoms in ^2D and ^2P excited states.**



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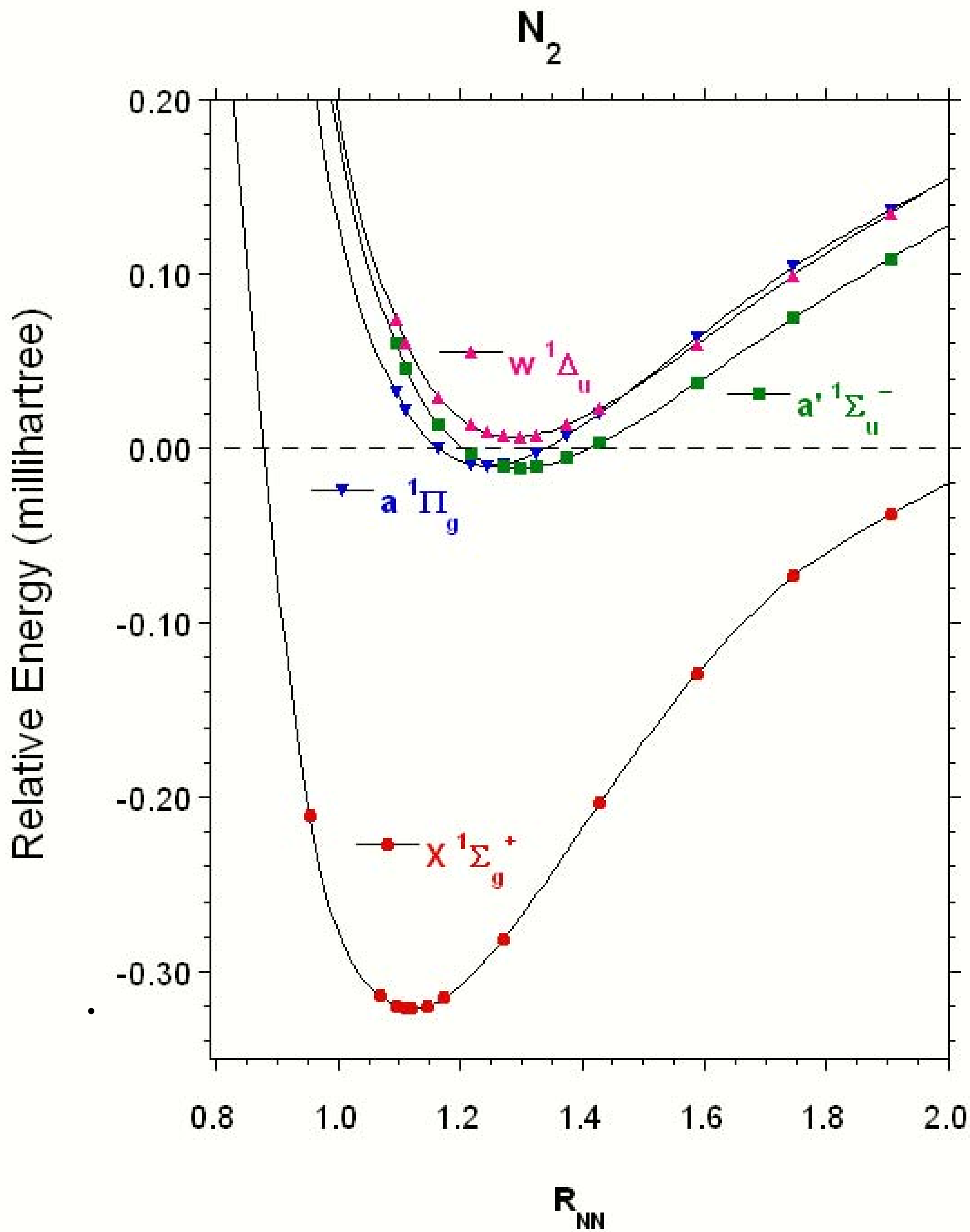
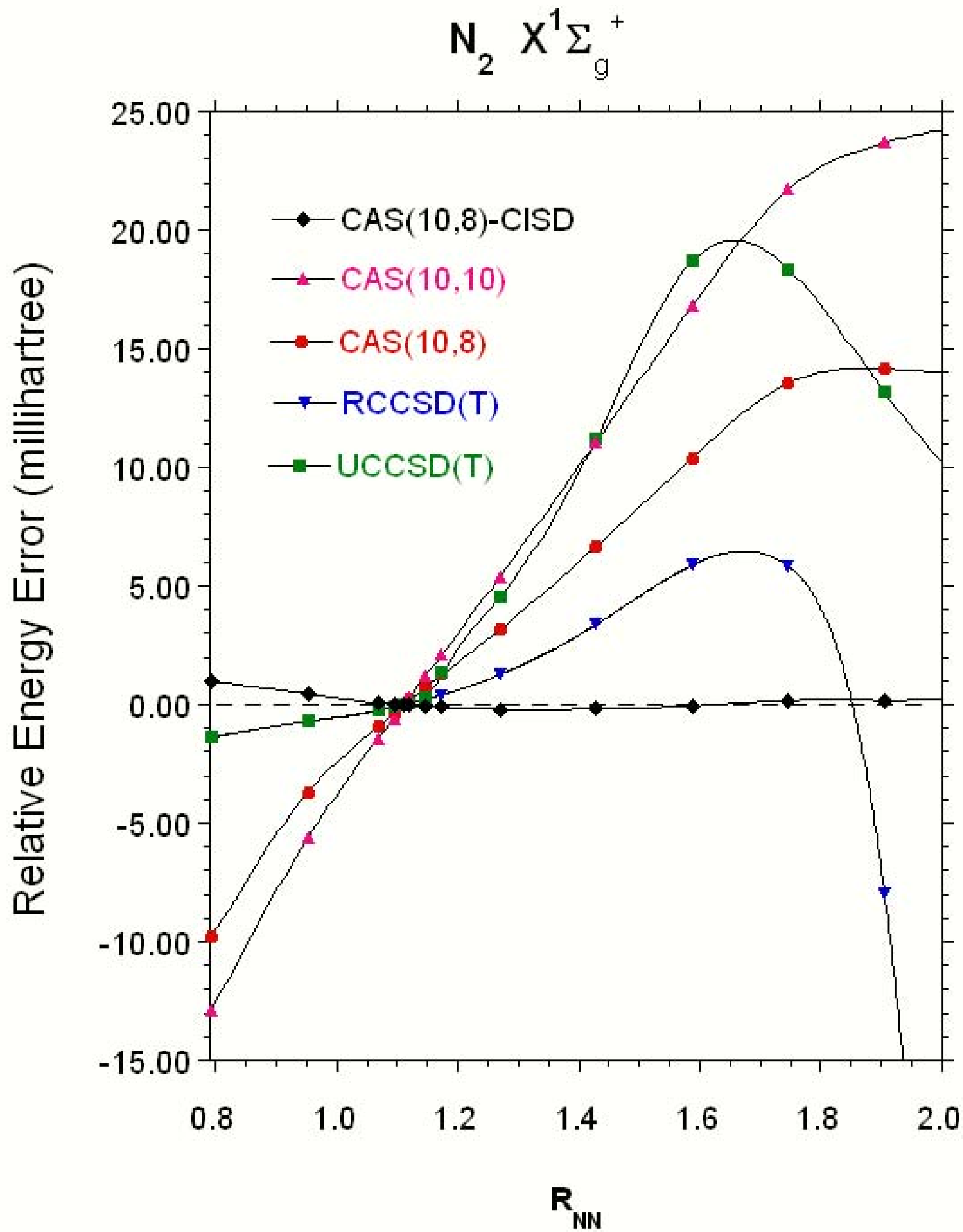
Benchmarks

The **FCI/cc-pVDZ** energies of low-lying states of N_2 [H. Larsen, J. Olsen, P Jørgensen, and O. Christiansen, *J. Chem. Phys*. **113**, 6677 (2000)] provide benchmarks for calibration of model chemistry candidates.



Model

The error in the energy of the ground state of N_2, relative to the energy at the equilibrium bond length. Note that the Multi-reference CAS-CISD is far more accurate than CCSD(T).



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The error in the energy of the ground state of N_2, relative to the Full CI energy is insensitive to bond length, but a constant size-consistency correction must be made for comparisons with atoms.

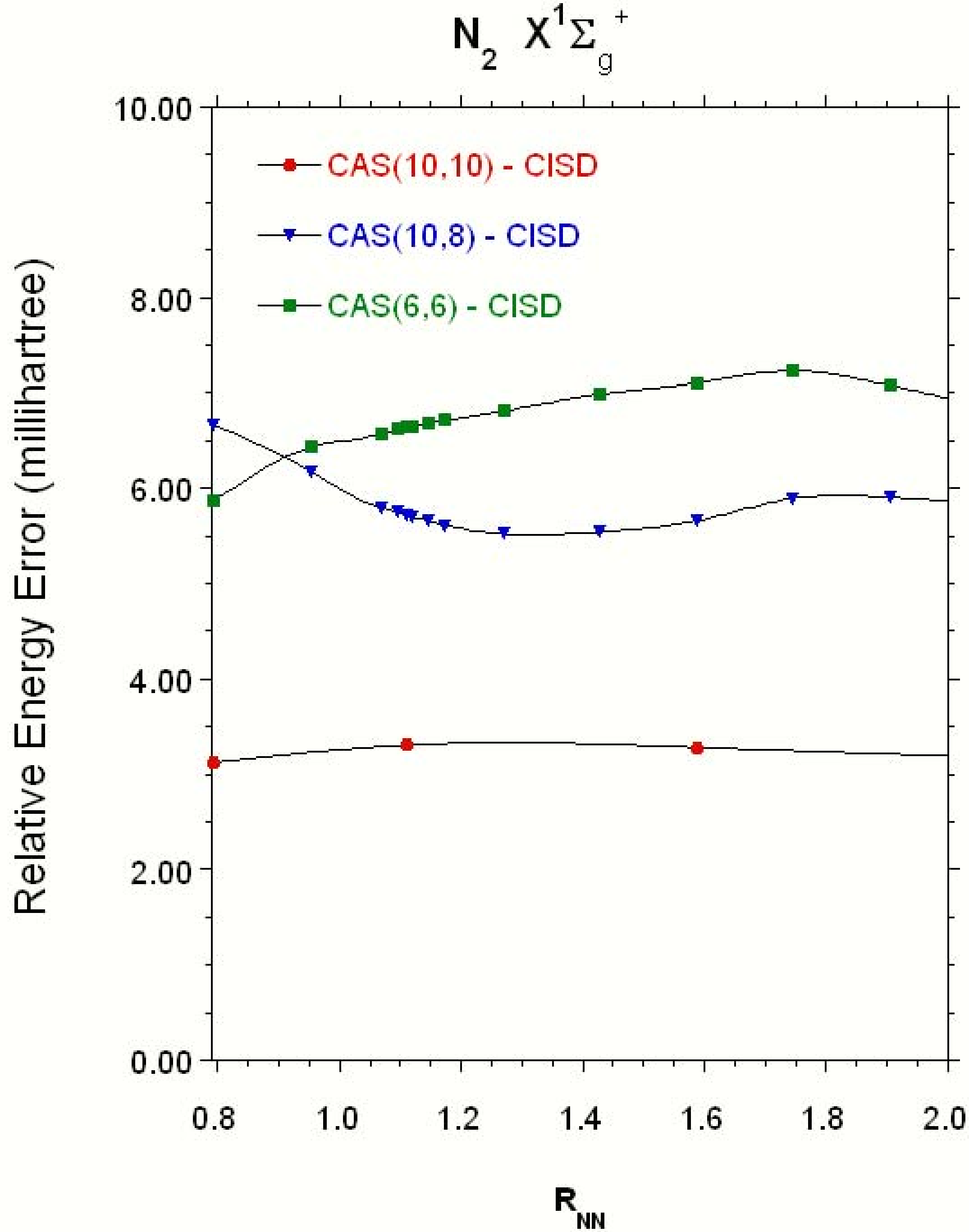

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Table I. The effect of **state averaging** on CASCF and CASSCF-CISD

State	R_{NN} (Å)	Basis Set	N_{root}=1 (E_h)	N_{root}=6 (E_h)	ΔE (mE_h)
			CAS(6_{e-},6_{Orb})		
$X^1\Sigma_g^+$	1.10	2ZaP	-109.1045238	-109.0781418	26.3820
		3ZaP	-109.1251169	-109.0979344	27.1825
$A^3\Sigma_u^+$	1.27	2ZaP	-108.8740932	-108.8606554	13.4378
		3ZaP	-108.8898435	-108.8761258	13.7177
			CAS(6_{e-},6_{Orb}) – CISD		
$X^1\Sigma_g^+$	1.10	2ZaP	-109.2896344	-109.2885919	**1.0425**
$A^3\Sigma_u^+$	1.27	2ZaP	-109.0736612	-109.0733565	**0.3047**

Table II. Calculated N_2 cc-pVDZ **excitaton energies** (mE_h).

RNN(Å)	Excitation	CAS(6,6)	CAS(6,6)-CISD	FCI
1.1113	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	**404.8**	**345.6**	**343.2**
	$\rightarrow a'\,^1\Sigma_u^-$	**375.9**	**367.9**	**367.0**
	$\rightarrow w\,^1\Delta_u$	412.1	383.5	381.7
1.2700	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	313.8	274.6	272.2
	$\rightarrow a'\,^1\Sigma_u^-$	280.6	271.6	270.6
	$\rightarrow w\,^1\Delta_u$	336.9	290.3	288.2
1.4288	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	252.8	226.7	223.4
	$\rightarrow a'\,^1\Sigma_u^-$	215.9	207.0	206.2
	RMS Error	**35.3**	**2.0**	

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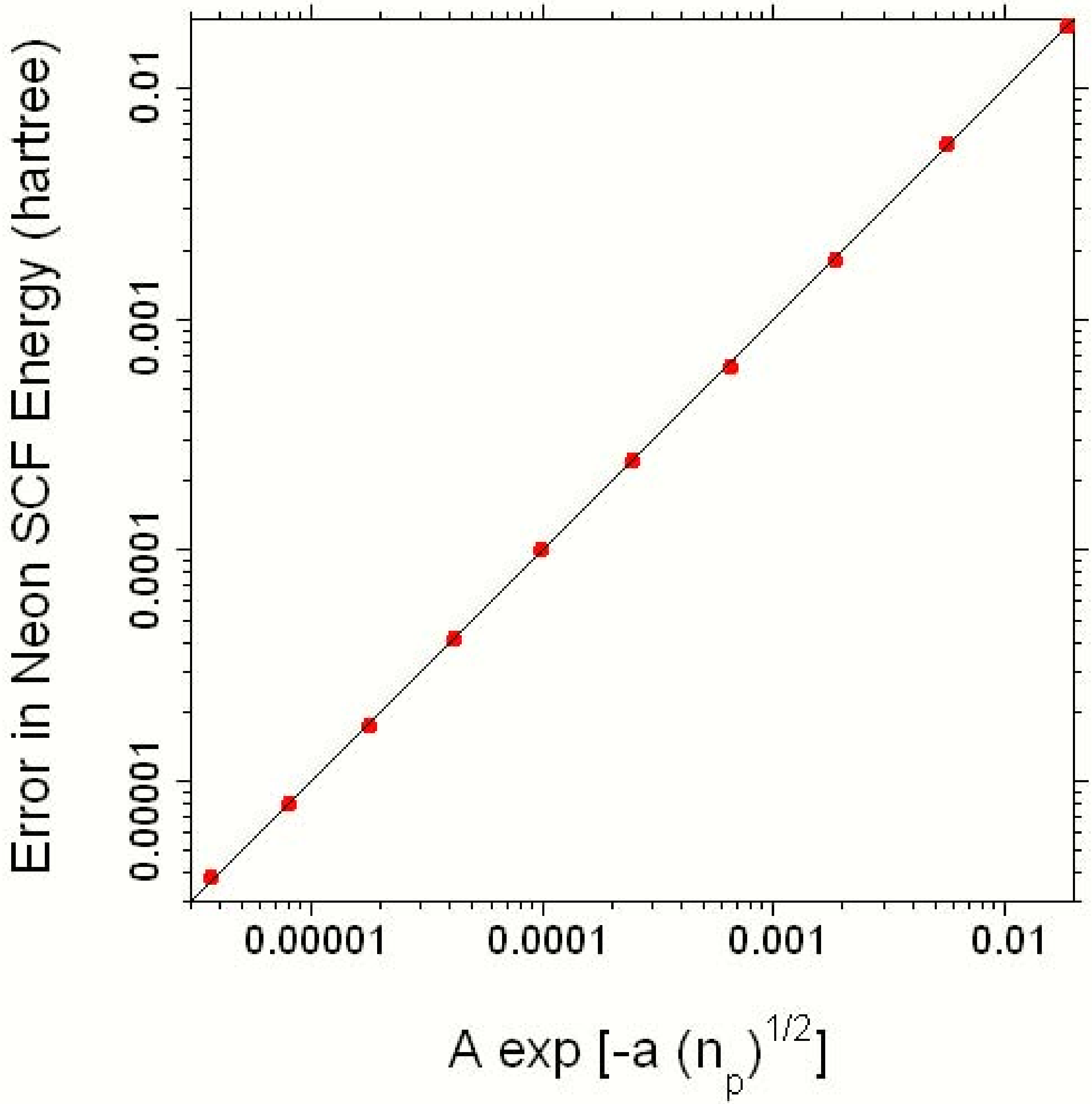
The **SCF** energy converges to the **CBS** (complete basis set) limit as the exponential of the square-root of the number of Gaussian basis functions.



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$$E_{SCF\ Limit} \cong E(n_2) + \{\exp[a(n_1)^{1/2} - a(n_2)^{1/2}] - 1\}^{-1} \{E(n_2) - E(n_1)\}$$

Table III. Linear SCF extrapolation parameters for the neon atom.

n_1	n_2	$\{\exp[a(n_1)^{1/2} - a(n_2)^{1/2}] - 1\}^{-1}$
5	6	0.426
6	7	0.490
7	8	0.551
8	9	0.609
6	**8**	**0.132**
8	**10**	**0.178**
10	**12**	**0.220**
12	**14**	**0.262**

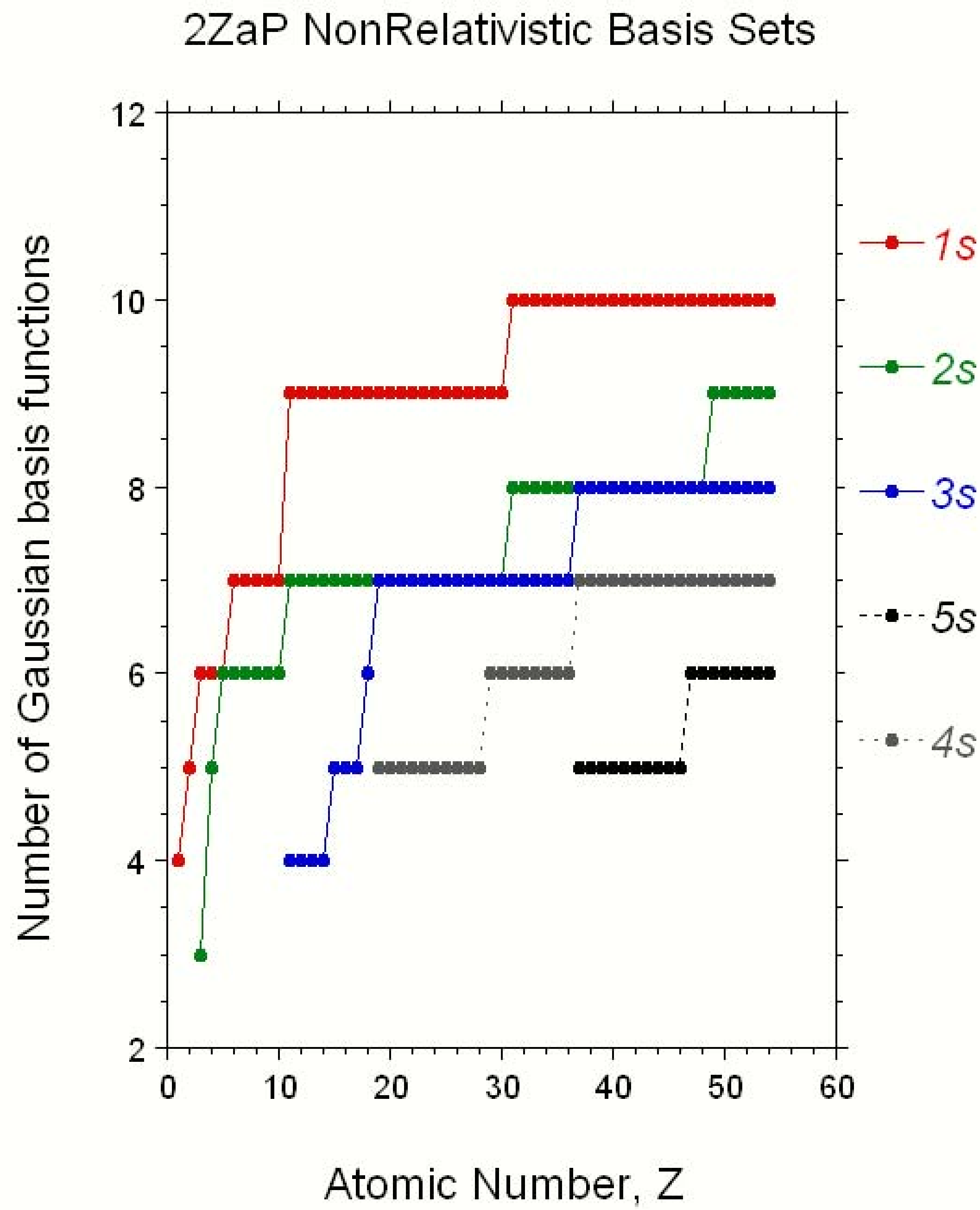
Table IV. The convergence of the N_2 SCF anisotropy energy (hartree) with the number of polarization functions in the basis set.

Basis Set	E_{SCF}	$\Delta E_{SCF}(n)$	E_{SCF} Error	Extrapolation Factor[a]
16s10p	-108.910331		0.082734	
16s10p1d	-108.981649	-0.071318	-0.011416	
16s10p2d1f	-108.991667	-0.010018	-0.001398	**0.139**
16s10p3d2f1g	-108.992847	-0.001180	-0.000218	**0.184**
16s10p4d3f2g1h	-108.993025	-0.000178	-0.000040	**0.22**
16s10p5d4f3g2h1i	-108.993057	-0.000032	-0.000008	**0.25**
SCF Limit **=**	-108.993065			

a. Factor = E_{SCF} Error(n) / $\Delta E_{SCF}(n)$

The nZaP BasisSets

The number of Gaussian primitives in the 2ZaP basis sets was selected to give a constant, *1 millihartree, SCF error per electron*. The 3ZaP basis sets each contain two more primitives of each angular momentum. The 4ZaP basis sets include an additional two, etc.



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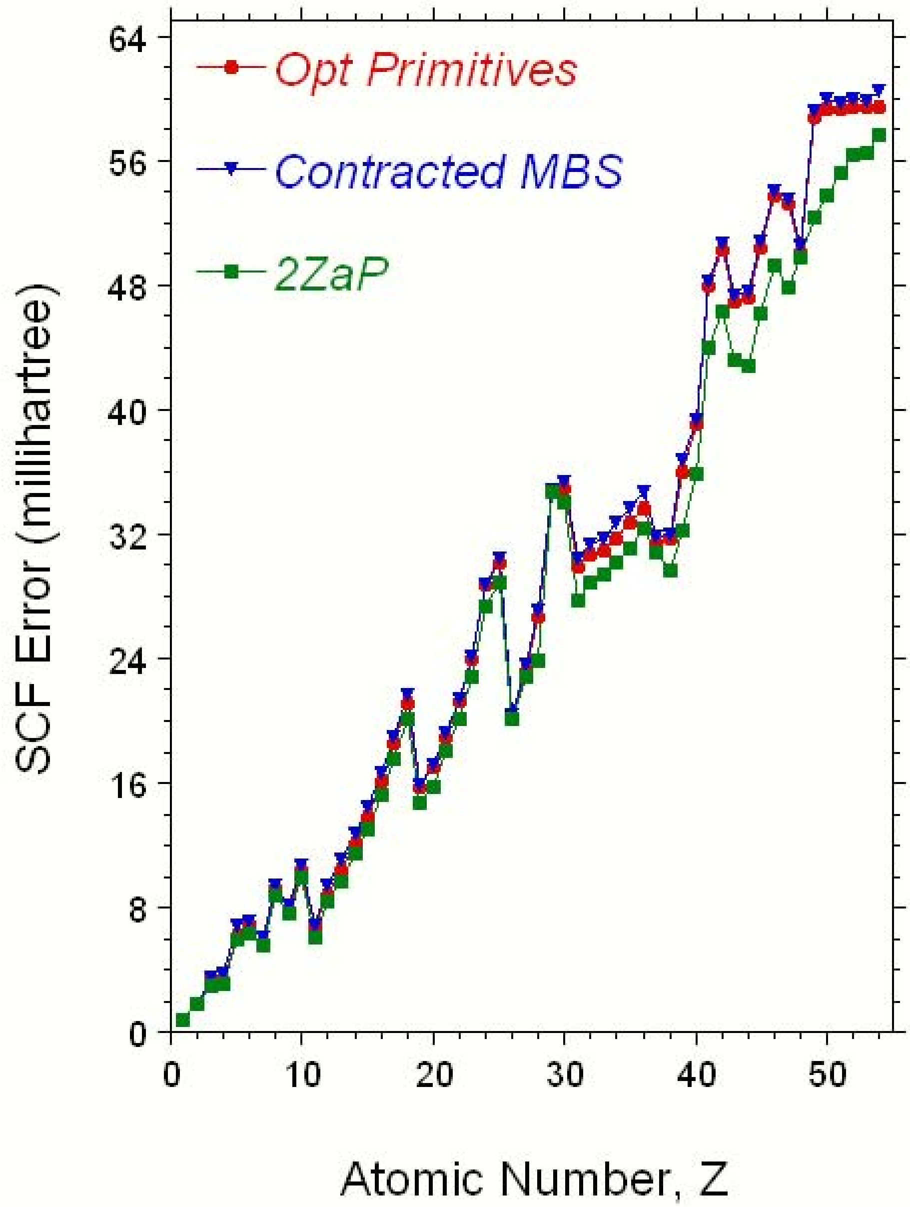
The nZaP BasisSets

The contracted nZaP basis sets are similar in structure to the cc-pVnZ basis sets, but with *diffuse valence functions added*. The number of primitives in each contracted function is sufficient to prevent contraction from significantly raising the SCF energy. All “correlation primitives” (*valence and polarization*) were optimized at the MP2 level.



UHF energies mimic the basis set convergence of CASSCF energies, but ROHF energies do not.

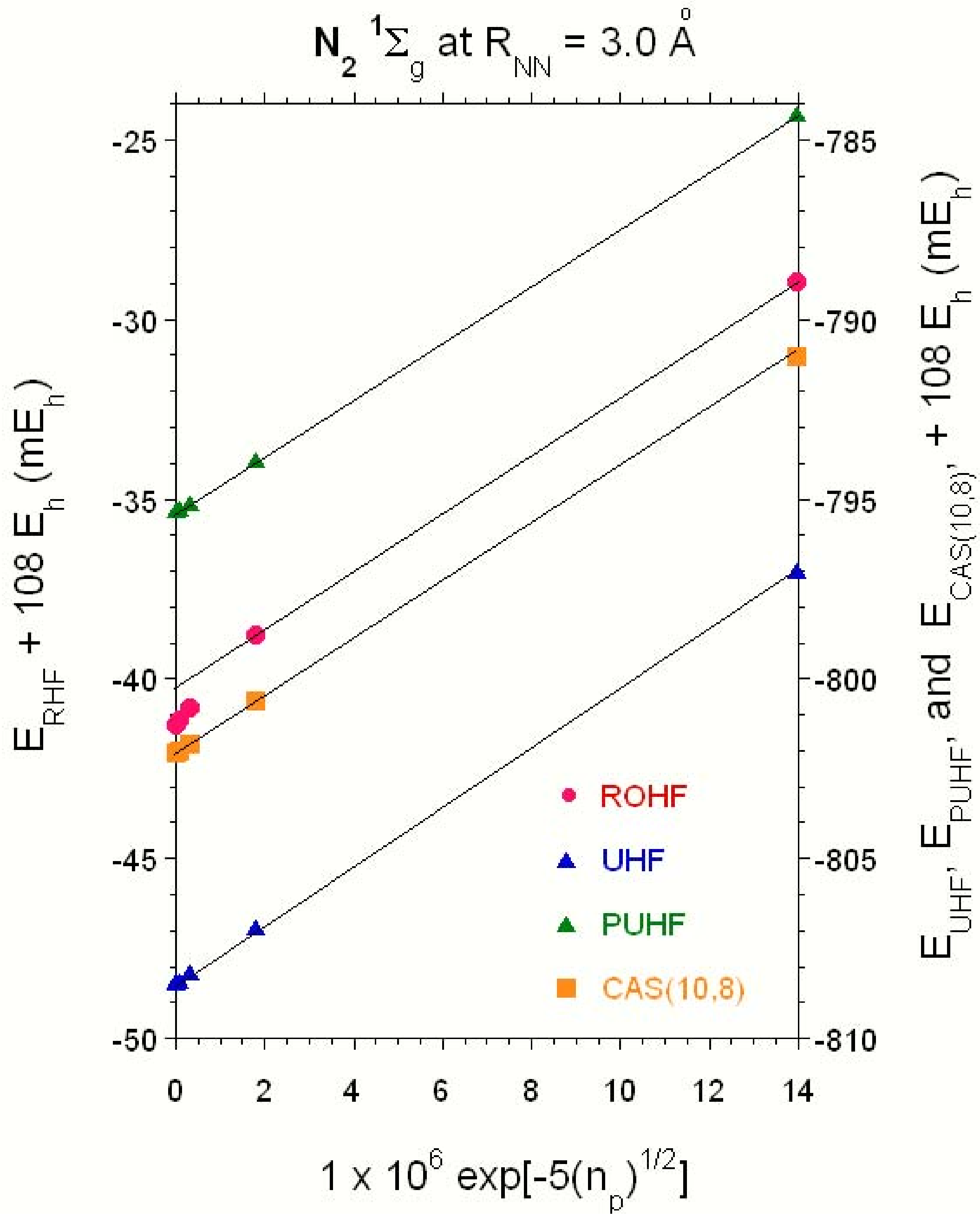


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Table V. Basis set convergence of CASSCF and UHFSCF as a function of geometry.

R_{NN} (Å)	Basis Set	CAS(6,6) (E_h)	ΔE (mE_h)	$\Delta(\Delta E)_R$ (mE_h)	UHF (E_h)	ΔE (mE_h)	$\Delta(\Delta E)_R$ (mE_h)
1.09	2ZaP	-109.1035124			-108.9687667		
	3ZaP	-109.1246270	-21.1146	0.5215	-108.9903071	-21.5404	0.4654
	4ZaP	-109.1279935	-3.3665	0.1042	-108.9935983	-3.2912	0.0966
	5ZaP	-109.1288265	-0.8330	0.0213	-108.9944093	-0.8110	0.0198
	6ZaP				-108.9945297	-0.1204	0.0013
1.10	2ZaP	-109.1045238			-108.9674580		
	3ZaP	-109.1251169	**-20.5931**	**0.4819**	-108.9885330	**-21.0750**	**0.4264**
	4ZaP	-109.1283792	**-3.2623**	**0.0978**	-108.9917276	**-3.1946**	**0.0898**
	5ZaP	-109.1291909	**-0.8117**	**0.0204**	-108.9925188	**-0.7912**	**0.0189**
	6ZaP				-108.9926379	-0.1191	0.0011
1.11	2ZaP	-109.1049575			-108.9655455		
	3ZaP	-109.1250687	-20.1112	0.4447	-108.9861941	-20.6486	0.3898
	4ZaP	-109.1282332	-3.1645	0.0917	-108.9892989	-3.1048	0.0833
	5ZaP	-109.1290245	-0.7913	0.0195	-108.9900712	-0.7723	0.0181
	6ZaP				-108.9901892	-0.1180	0.0011

$$E_{CAS}(CBS) \cong E_{CAS}(3ZaP)$$

$$+1.2\times\left[E_{UHF}(4ZaP)-E_{UHF}(3ZaP)\right]$$

$$\times\left[\frac{E_{CAS}(3ZaP)-E_{CAS}(2ZaP)}{E_{UHF}(3ZaP)-E_{UHF}(2ZaP)}\right]$$

Table VI. Calculated Full Valence CASSCF energies (hartree au).

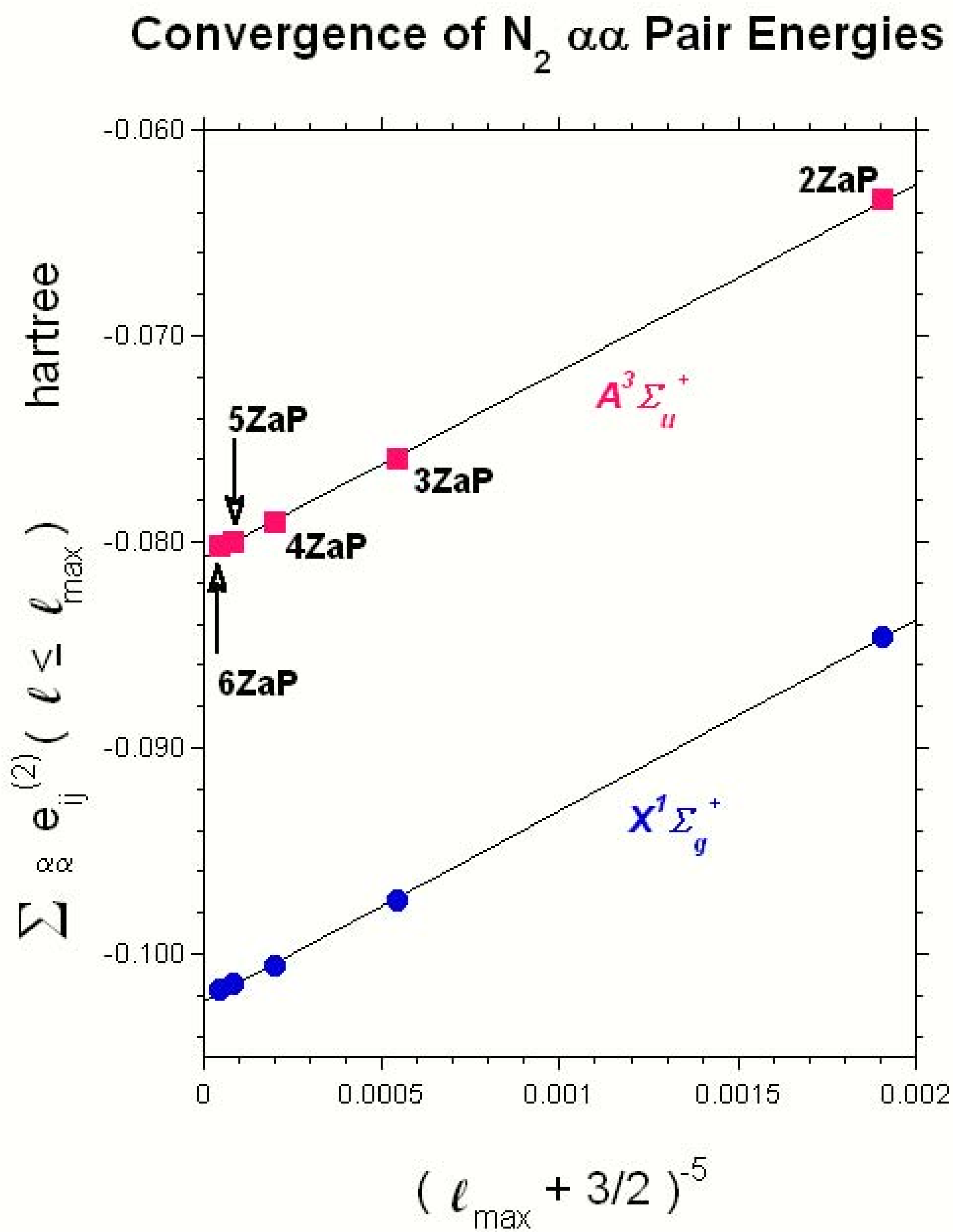
	2ZaP	3ZaP	4ZaP	5ZaP	6ZaP	Limit
C_2 $X^1\Sigma_g^+$	-75.6233832	-75.6412898	-75.6437447	-75.6442121	-75.6442908	-75.6443188
C_2 $a^3\Pi_u$	-75.6073350	-75.6230710	-75.6251470	-75.6255495	-75.6256266	-75.6256541
C_2 $b^3\Sigma_g^-$	-75.5777931	-75.5941905	-75.5962600	-75.5966964	-75.5967840	-75.5968152
C_2 $A^1\Pi_u$	-75.5627890	-75.5788475	-75.5809697	-75.5813798	-75.5814615	-75.5814906
CN $X^2\Sigma^+$	-92.3544025	-92.3730997	-92.3761806	-92.3766716	-92.3767524	-92.3767812
CO $X^1\Sigma^+$	-112.8946223	-112.9181416	-112.9218328	-112.9224855	-112.9226137	-112.9226594
N_2 $X^1\Sigma_g^+$	-109.1166132	-109.1373292	-109.1406653	-109.1414826	-109.1415931	-109.1416324
NO $X^2\Pi_i$	-129.3892421	-129.4106758	-129.4138042	-129.4143983	-129.4144941	-129.4145282
O_2 $X^3\Sigma_g^-$	-149.7411441	-149.7681917	-149.7713131	-149.7719475	-149.7720640	-149.7721055
O_2 $a^1\Delta_g$	-149.7059304	-149.7327122	-149.7358092	-149.7364403	-149.7365522	-149.7365920
O_3 X^1A_1	-224.5478659	-224.5938866	-224.5991383	-224.6002546	-224.6004950	-224.6005806
OH $X^2\Pi$	-75.4325178	-75.4440618	-75.4456305	-75.4458720	-75.4459251	-75.4459441
OH $A^2\Sigma^+$	-75.2670507	-75.2808979	-75.2825953	-75.2828559	-75.2829216	-75.2829450
RMS Error	**0.0224147**	**0.0030328**	**0.0005829**	**0.0001180**	**0.0000310**	

Table VII. Extrapolated Full Valence CASSCF energies (hartree au).

		Error	
	3ZaP	4ZaP	5ZaP
$C_2\ X^1\Sigma_g^+$(Re)	-0.0001705	0.0000255	-0.0000059
$C_2\ a^3\Pi_u$(Re)	-0.0001753	0.0000582	0.0000012
$C_2\ b^3\Sigma_g^-$(Re)	-0.0002094	0.0000064	-0.0000040
$C_2\ A^1\Pi_u$(Re)	-0.0000459	0.0000176	0.0000026
CN $X^2\Sigma^+$(Re)	-0.0001536	0.0000366	-0.0000031
$N_2\ X^1\Sigma_g^+$(Re)	-0.0005054	-0.0001428	-0.0000276
NO $X^2\Pi_i$(Re)	-0.0001124	-0.0001120	-0.0000175
$O_2\ X^3\Sigma_g^-$(Re)	0.0000564	-0.0001285	-0.0000186
$O_2\ a^1\Delta_g$(Re)	-0.0000230	-0.0001280	-0.0000168
OH $X^2\Pi$(Re)	-0.0000524	-0.0000353	-0.0000136
OH $A^2\Sigma^+$(Re)	0.0000168	-0.0000603	-0.0000194
RMS Error	**0.0002327**	**0.0000956**	**0.0000245**
Before Extrap	**0.0030328**	**0.0005829**	**0.0001180**

MP2 CBS Limit

The $\alpha\alpha$ second-order Møller-Plessett electron pair correlation energies converge to the CBS limit as the inverse fifth power of the maximum angular momentum included in the basis set.



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MP2 CBS Limit

The αβ second-order Møller-Plessett electron pair correlation energies converge to the CBS limit as the inverse **third** power of the maximum angular momentum included in the basis set.

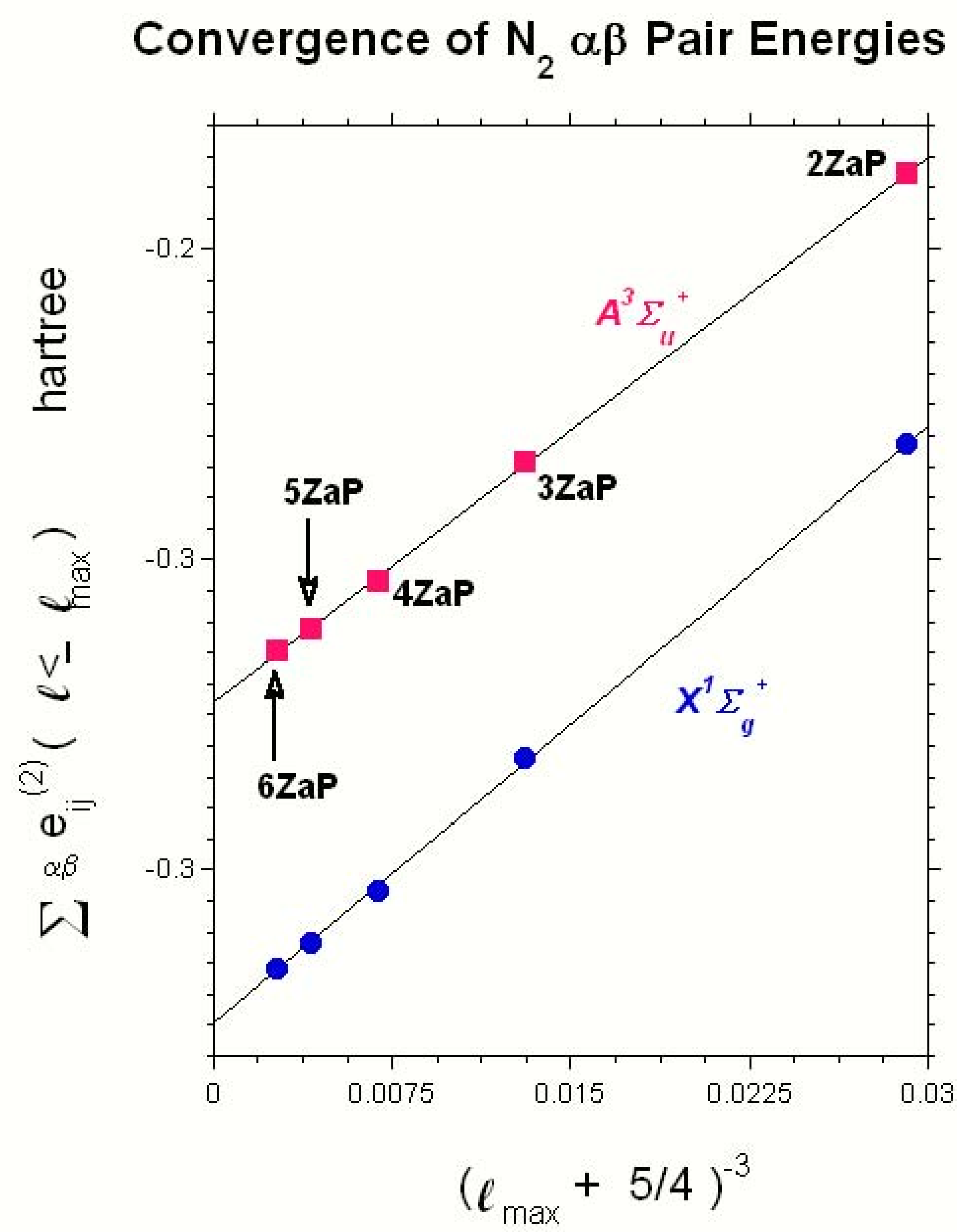

Table VIII. The basis set convergence of dynamic correlaton energy.

State	Basis Set	$E^{(2)}$ (mE_h)	$\Delta E^{(2)}$ (mE_h)	$E_{CAS\text{-}CISD} - E_{CAS}$ (mE_h)	$\Delta(E_{CAS\text{-}CISD} - E_{CAS})$ (mE_h)
$X^1\Sigma_g^+$	2ZaP	-316.0189		-181.9089	
1.10Å	3ZaP	-379.3504	**-63.3315**	-244.4998	**-62.5909**
	4ZaP	-403.7559			
	5ZaP	-413.3317			
	6ZaP	-417.4648			
	CBS Limit	-426.90			
$A^3\Sigma_u^+$	2ZaP	-250.9989		-195.6356	
1.27Å	3ZaP	-310.1058	**-59.1069**	-255.0882	**-59.4526**
	4ZaP	-332.4087			
	5ZaP	-341.1121			
	6ZaP	-344.7652			
	CBS Limit	-353.59			

$$E_{CAS-CISD}(CBS) \cong E_{CAS-CISD}(3ZaP)$$

$$+\left[E^{(2)}(CBS) - E^{(2)}(3ZaP)\right]$$

$$\times\left[\frac{E_{CAS-CISD}(3ZaP) - E_{CAS-CISD}(2ZaP)}{E^{(2)}(3ZaP) - E^{(2)}(2ZaP)}\right]$$

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Table IX. Calculated CAS-CISD **geometries** (R_e in Å) for low-lying excited states of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\ ^1\Sigma_g^+$	1.1175	1.1039	1.0991	1.0977
$A\ ^3\Sigma_u^+$	1.3066	1.2951	1.2905	1.2866
$B\ ^3\Pi_g$	1.2314	1.2201	1.2152	1.2126
$W\ ^3\Delta_u$	1.2972	1.2859	1.2815	
$B'\ ^3\Sigma_u^-$	1.2955	1.2845	1.2800	1.2784
$a'\ ^1\Sigma_u^-$	1.2914	1.2805	1.2759	1.2755
$a\ ^1\Pi_g$	1.2390	1.2271	1.2213	1.2203
$w\ ^1\Delta_u$	1.2837	1.2728	1.2684	1.268
RMS Error	**0.0181**	**0.0066**	**0.0020**	

Table X. Calculated CAS-CISD harmonic **vibrational frequencies** (ω_e in cm^{-1}) for low-lying excited states of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\ ^1\Sigma_g^+$	2319.1	2345.2	2358.1	2358.57
$A\ ^3\Sigma_u^+$	1418.5	1439.7	1450.8	1460.64
$B\ ^3\Pi_g$	1707.4	1715.3	1727.4	1733.39
$W\ ^3\Delta_u$	1482.0	1499.1	1508.9	$1501._4$
$B'\ ^3\Sigma_u^-$	1494.5	1509.9	1518.9	1516.88
$a'\ ^1\Sigma_u^-$	1508.6	1528.4	1538.8	1530.25
$a\ ^1\Pi_g$	1648.2	1686.1	1696.4	1694.21
$w\ ^1\Delta_u$	1543.5	1561.3	1571.3	1559.26
RMS Error	**31.1**	**12.1**	**7.3**	

Table XI. Calculated CAS-CISD **excitation energies** (Ev) of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\ {}^1\Sigma_g^+ \rightarrow$				
$A\ {}^3\Sigma_u^+$	5.843	6.093	6.192	6.224
$B\ {}^3\Pi_g$	7.275	7.397	7.447	7.392
$W\ {}^3\Delta_u$	7.233	7.364	7.432	7.415
$B'\ {}^3\Sigma_u^-$	8.067	8.230	8.265	8.217
$a'\ {}^1\Sigma_u^-$	8.427	8.471	8.407	8.450
$a\ {}^1\Pi_g$	8.547	8.653	8.562	8.590
$w\ {}^1\Delta_u$	8.932	9.008	8.927	8.939
RMS Error	**0.176**	**0.065**	**0.037**	

Table XII. Calculated CAS-CISD dissociation energies (Ev) of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\,^1\Sigma_g^+ \rightarrow$				
$A\,^3\Sigma_u^+$	5.857	6.093	6.192	6.224
$B\,^3\Pi_g$	7.256	7.397	7.447	7.392
$W\,^3\Delta_u$	7.301	7.364	7.432	7.415
$B'\,^3\Sigma_u^-$	8.063	8.230	8.265	8.217
$a'\,^1\Sigma_u^-$	8.417	8.471	8.407	8.450
$a\,^1\Pi_g$	8.537	8.653	8.562	8.590
$w\,^1\Delta_u$	8.914	9.008	8.927	8.939
RMS Error	**0.167**	**0.065**	**0.037**	

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